# Solvent Effects in Radical Copolymerization between Hydrophilic and Hydrophobic Monomers; 2-Hydroxyethyl Methacrylate and Lauryl Methacrylate

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ABSTRACT:    The radical copolymerization of 2-hydroxyethyl methacrylate (HEMA, $M_1$) and
lauryl methacrylate (LMA, $M_2$) was investigated at 60°C with AIBN in various solvents including
benzene, tetrahydrofuran, tert-butylalcohol, and dimethylformamide. HEMA was found to have
an abnormally high, apparent monomer reactivity ratio in benzene, $r_1 = 11.2$, corresponding to its
high aggregation tendency in this solvent as a result of hydrogen-bonding. The apparent reactivity
ratios are more or less close to azeotropic unity in the other solvents. The solution behavior of
monomers is proposed as a factor in the copolymerization between hydrophilic and hydrophobic
monomers.
    KEY WORDS    Solvent Effect / Radical Copolymerization / 2-Hydroxy-
        ethyl Methacrylate / Lauryl Methacrylate / Hydrophilic–Hydrophobic
        Copolymers / Hydrogen-Bonding Aggregation / Monomer Reactivity
        Ratio /

Increasing attention is currently being directed to the synthesis of copolymers carrying both hydrophilic and hydrophobic segments for application to various functional polymers. This trend is further stimulated by the recent development of the macromonomer ('macromer') technique for preparing well-defined graft copolymers. The copolymerization between hydrophilic and hydrophobic monomers, however, involves certain complications arising from the very different solution properties of the monomers. In fact, acid monomers such as acrylic acid and methacrylic acid have been found to have apparently higher reactivities in copolymerizations with methyl methacrylate or styrene in nonpolar solvents compared to those in polar solvents.[1–6] This is accounted for by aggregation of the acid monomers through hydrogen-bonding. Selective solvation of a growing chain end by the acid monomer was proposed by Plochocka and Harwood[5] for styrene-acrylic acid system based on the fact that the monomer sequence (triad) distribution, determined by 300 MHz ^{1}H NMR, was found to be the same for copolymers of the same composition, irrespective of the solvents used in the preparation.

2-Hydroxyethyl methacrylate (HEMA) is widely used as a typical hydrophilic monomer with a nonelectrolytic hydroxyl group. Although its copolymerization has been reported in a limited cases,[7–14] the available monomer reactivity ratios are somewhat mis-

**Table I.** Selected radical-copolymerization parameters of HEMA

| $M_1$ | $M_2$ | Conditions | $r_1$ | $r_2$ | Ref |
|-------|-------|------------|-------|-------|-----|
| HEMA | MMA[a] | BPO, bulk, 60°C | 1.054 | 0.296 | 7 |
| HEMA | MMA[a] | AIBN, DMF ([M]=0.3 mol l^{-1}), 60°C | 0.66 | 0.84 | 8 |
| HEMA | MMA[a] | — | 1.25 | 0.89 | 9 |
| HEMA | MMA[a] | Calcd from $Q$, $e$ | 1.18 | 0.85 | 10 |
| HEMA | St[b] | AIBN, bulk, 60°C | 0.85 | 0.33 | 8 |
| HEMA | St[b] | — | 0.65 | 0.57 | 9 |
| HEMA | St[b] | Calcd from $Q$, $e$ | 0.65 | 0.56 | 10 |
| HEMA | SMA[c] | AIBN, THF ([M] $\cong$ 40 wt%), 60°C | 3.02 | 0.76 | 11 |
| HEMA | PSt-MA[d] | AIBN, DMF, ([M]= 10 wt%), 60°C | $1.7 \pm 0.4$ | — | 12 |
| HEMA | PSt-MA[e] | DIPC,[f] DMF ([M] $\cong$ 20 wt%), 60°C | 2.0—2.3 | — | 13 |

[a] Methyl methacrylate. [b] Styrene. [c] Stearyl methacrylate.
[d] Methacrylate-ended polystyrene, $M_n = 3180$.
[e] Methacrylate-ended polystyrene, $M_n = 14000$ or $23000$.
[f] Diisopropyl peroxydicarbonate.

leading in that they significantly differ depending on the authors and/or conditions, as exemplified in Table I. This fact by itself suggests the complicated nature of the copolymerization including HEMA. A similar complication was recently found for the rate of copolymerization of HEMA with styrene.[15]

To understand the abnormal behavior of HEMA, we examine in this paper copolymerization with a typical hydrophobic monomer, lauryl methacrylate (LMA) in various solvents, together with some physico-chemical properties of the monomers. The results are discussed in terms of possible factors influencing the copolymerization between hydrophilic and hydrophobic monomers.

## EXPERIMENTAL

Monomers, HEMA and LMA, were distilled over calcium hydride under a reduced pressure of argon. Solvents were purified and distilled by usual procedures. $\alpha,\alpha'$-Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

Copolymerization was conducted in a flask equipped with a three-way cock with a silicone septum. Monomers, AIBN, solvent, and non-adecane, which served as an internal standard for gas chromatography, were charged into the flask, degassed by freeze-thaw cycles, charged with argon gas, and then placed in an oil bath at $60 \pm 1°C$. Consumption of the monomers was monitored by a gas chromatograph, Yanaco G-180, equipped with a column of PEG 20M, 2.25 or 3 m length, and a TCD or FID detector. The column temperature was 190 or 200°C. Copolymer compositions were calculated from the monomer concentration–time plots at a point of about 10% total conversion so as to avoid any ambiguity in the reading of the consumption rate at zero conversion. The copolymerization system was homogeneous up to this conversion in all cases investigated.

Some copolymers were prepared independently under the same conditions, precipitated out of a mixture of water and methanol (20 : 80, v/v), and dried *in vacuo*. ¹H-NMR spectra were recorded on a JEOL JNM-PMX 60 spectrometer, and gel permeation chromatography (GPC) was carried out on a JASCO

TRIROTAR-III equipped with a column A-803 with a tetrahydrofuran solution at a flow rate of 1 ml min$^{-1}$ at 40°C, monitored by a RI detector, Shodex SE-11.

The freezing point of a monomer solution for cryoscopic determination of aggregation was read on a cooling–curve (temperature–time plot) made with a mechanically stirred solution in a double-wall glass tube cooled outside with a dry ice-acetone mixture. The temperature was read with a standardized thermometer inserted into the solution. Heat of solution was measured on a twin calorimeter, TIC-2D, Tokyo Riko Co., Ltd., at a molar ratio of monomer to solvent greater than 150 as an approximation of infinite dilution. Temperature of measurement was 20.5°C in benzene, tetrahydrofuran (THF), and dimethylformamide (DMF), and 26.0°C in *tert*-butylalcohol ($^t$BuOH). The error of the measurement was estimated to be within ±5%.

## RESULTS AND DISCUSSION

The copolymerization of HEMA and LMA was conducted at 60°C with AIBN, at a total monomer concentration of 0.5 mol l$^{-1}$ in benzene, THF, $^t$BuOH, and DMF. Figure 1 shows the monomer–copolymer composition curves obtained by monitoring the monomer consumption by gas chromatography. Clearly, the reactivity of HEMA is abnormally high in benzene, while the compositions are more or less close to the azeotrope line in the other solvents. Monomer reactivity ratios were estimated by the method of Kelen and Tüdös,[16] and the results are given in Table II. Here again, HEMA is highly reactive, with $r_1$ amounting to 11.2, while the reactivity ratios in the other solvents are scattered around unity. It should be noted that the composition curves in Figure 1 as well as the Kelen–Tüdös plots were normal in all cases, thus apparently fitting the conventional, terminal copolymerization model.
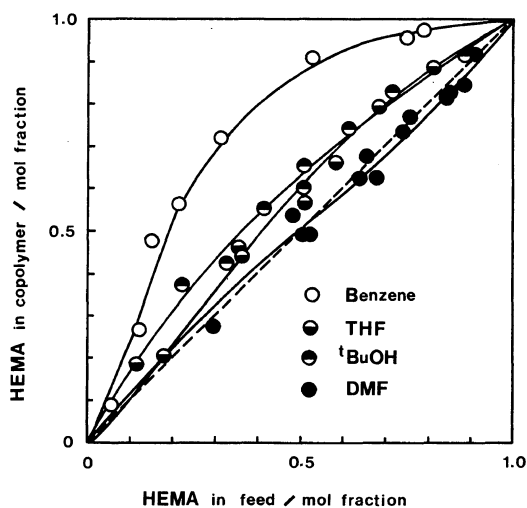


**Figure 1.** Composition curves for copolymerizations of HEMA and LMA in various solvents. Total monomer concentration = 0.5 mol l$^{-1}$.

**Table II.** Monomer reactivity ratios of copolymerizations of HEMA ($M_1$) and LMA ($M_2$) in various solvents[a]

| Solvent | $r_1$ | $r_2$ |
|---|---|---|
| Benzene | 11.2 ± 2.8 | 0.7 ± 0.3 |
| THF | 2.0 ± 0.3 | 1.0 ± 0.3 |
| $^t$BuOH | 1.6 ± 0.3 | 0.5 ± 0.2 |
| DMF | 0.8 ± 0.1 | 0.8 ± 0.4 |

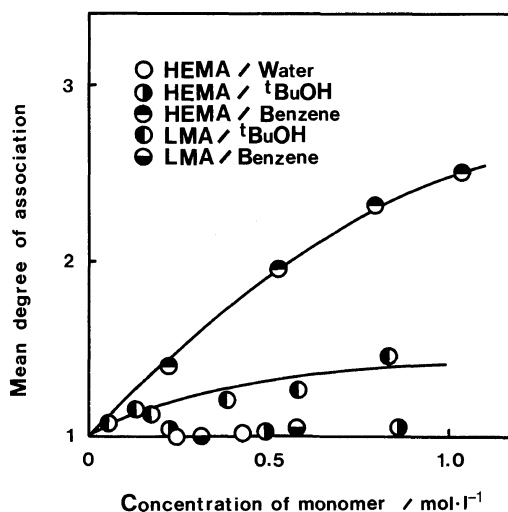[a] Errors indicated are 95% confidence limits.

Some copolymers were independently prepared, isolated, and characterized by $^1$H NMR and GPC, and the results are summarized in Figure 2 and Table III. These copolymers were all soluble in chloroform, a nonsolvent for a HEMA homopolymer. The NMR spectrum in CDCl$_3$ showed slightly sharper peaks of lauryl methylene and $\omega$-methyl protons, at $\delta$ 1.2 and 1.0, respectively, compared to those of HEMA oxyethylene protons at about $\delta$ 4.0, while exactly the reverse trend was observed in a spectrum in a mixture of CDCl$_3$ and CD$_3$OD (1 : 1, v/v). This indicates that LMA units constitute a relatively more mobile segment in the former solvent, while HEMA units do so in the latter solvent. The peak areas, however, are normal in that the copolymer compositions estimated

**Table III.** Characterization of HEMA ($M_1$)–LMA ($M_2$) copolymers

| Polymn. solvent | HEMA mol% in feed | Polymn. | | HEMA mol% in copolymer | | | GPC data (rel to PSt) | |
| | | time | Yield | | from NMR in | | | |
| | | | | Calcd from $r_1$, $r_2$ | CDCl$_3$ | CDCl$_3$ +CD$_3$OD | $M_n \times 10^4$ | $M_w/M_n$ |
| | | min | wt% | | | | | |
| Benzene | 10 | 60 | 9 | 22 | 15 | — | — | — |
| Benzene | 20 | 35 | 15 | 50 | 48 | 45 | 4.2 | 1.8 |
| Benzene | 33 | 21 | 17 | 75 | 76 | — | 3.9 | 2.2 |
| THF | 39 | 46 | 14 | 47 | 43 | 49 | 2.3 | 2.5 |
| 'BuOH | 37 | 20 | 7 | 50 | 41 | 37 | 4.3 | 2.0 |
| DMF | 50 | 11 | 19 | 50 | 41 | 40 | 2.2 | 2.5 |
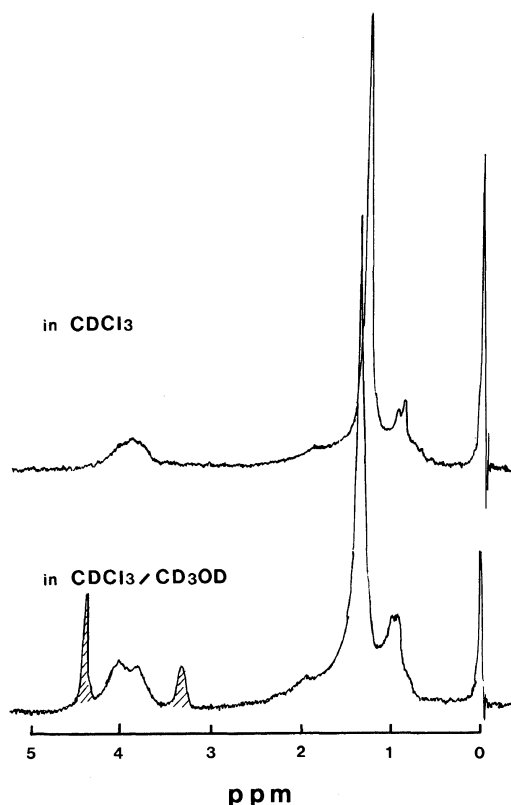


**Figure 2.** $^1$H NMR spectra of a HEMA-LMA copolymer (from copolymerization in benzene at a molar ratio HEMA/LMA=20/80) in CDCl$_3$ and in CDCl$_3$-CD$_3$OD (1:1, v/v).



**Figure 3.** Mean degree of association of HEMA and LMA in various solvents.

polystyrene graft copolymers, the peak of HEMA oxyethylene protons was absent in the spectrum, possibly as a result of a micelle formation with a core of HEMA segments in chloroform.[12] All these observations clearly support that the HEMA-LMA copolymers are qualitatively random in sequence distribution. No difference was also found in the $^1$H NMR spectra of the copolymers in Table III, depending on the solvent for copolymerization.

The apparently high reactivity of HEMA suggested an aggregation of this monomer in benzene, and thus some physico-chemical properties were examined. Figure 3 shows the
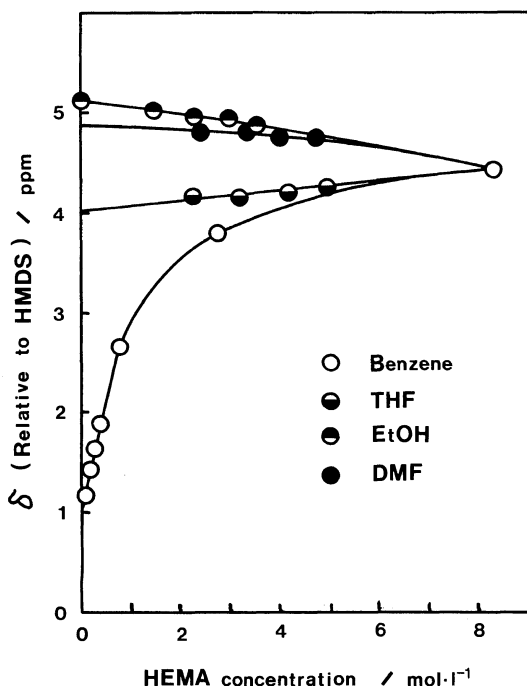
from the relative areas of the respective peaks were the same, irrespective of the solvents for the NMR measurements.[18] This is in sharp contrast with the fact that, for polyHEMA-

**Figure 4.** Hydroxyl proton chemical shifts of HEMA in various solvents.

**Table IV.** Heat of solution of HEMA and LMA in various solvents

| Solvent ($\varepsilon^a$) | $\Delta H$, kcal mol$^{-1b}$ | |
| --- | --- | --- |
| | HEMA | LMA |
| Benzene (2.28) | 2.7 | 0.78 |
| THF (7.58) | −0.053 | 0.41 |
| $^t$BuOH (12.5) | 0.19 | 2.7 |
| DMF (36.7) | −0.78 | 2.6 |

[a] Dielectric constant at 25°C.
[b] Negative values indicate exothermic heats of solution.

mean degree of association of the monomers, estimated cryoscopically. As expected, HEMA is clearly aggregated in benzene, while no association was found in water and in $^t$BuOH. In contrast, LMA shows some degree of association in the polar solvent, $^t$BuOH, but no association in benzene. The HEMA hydroxyl chemical shift in Figure 4 shows a very pronounced shift in benzene to a lower magnetic field with increasing concentration as compared to very small, linear shifts in the other solvents. This strongly supports the intermolecular aggregation of HEMA as a result of hydrogen-bonding. Heats of solution, $\Delta H$, of HEMA and LMA in the four solvents were measured by a twin calorimeter. The data in Table IV indicate a considerably high endothermic process of HEMA dissolved into benzene, supporting a corresponding high aggregation energy in this system. Relatively small values of $\Delta H$ in cases including HEMA in $^t$BuOH and in DMF, and LMA in benzene and in THF indicate no particular interactions

in these systems. LMA, when dissolved in $^t$BuOH and DMF, shows a rather high $\Delta H$, suggesting again some association, possibly due to van der Waals attraction between the long alkyl groups in these polar solvents.

By the above results, it is reasonable that the apparently high reactivity of HEMA in benzene results from the high tendency of aggregation in this system. The value of $r_1$ in benzene, however, is larger than those in the other solvents by a factor of 6 to 13, which is considerably higher than the mean degree of aggregation of HEMA, about 2.0 at 0.5 mol $l^{-1}$. Therefore, the increase in $r_1$ cannot be simply attributed to the increased local concentration as a result of only aggregation. Preferential solvation of the hydrophilic monomer around the active polymer radical, as proposed by Plochocka and Harwood,[5] is also a plausible explanation for the result. In spite of some association of LMA observed in $^t$BuOH and also possibly in DMF, $r_2$ values in Table II changed little with the solvent. The van der Waals interaction between the long alkyl groups may be relatively loose, long-ranged, and transient in nature, thus contributing little to the increase in local concentration of the double bonds or it may even lead to reduced reactivity of the double bond by making a hydrophobic environment or a steric repulsion about the reaction center. However, it is difficult to discuss further the respective values of $r_1$ and $r_2$ as well as the fact that the product $r_1 r_2$ is

greater than unity, unusual for a radical co-polymerization, in THF, a solvent with little specific interaction with and among the monomers.

At any rate, the monomer reactivity ratios in these systems do not necessarily have true meaning as defined by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, but should be taken as apparent ratios subject to change in local concentration and/or in reactivity of the double bond, depending on the condition. This situation may be, at least in part, responsible for the varying monomer reactivity ratios reported by different authors for the same nominal system. Copolymeri-zation in bulk or in a concentrated solution, particularly in nonpolar solvents, may be further complicated by possible change in ag-gregation and reactivity depending on feed composition. Evaluation of $r_1$ and $r_2$ from the $Q$–$e$ scheme would be almost meaningless in these systems.

The reactivity ratio of HEMA in copolym-erization with methacrylate-ended polysty-rene macromonomer ($r_1 = 1.7$ or $2.0$—$2.3$ in DMF, Table I)[12,13] is higher than that with a model monomer LMA ($r_1 = 0.8$ in DMF, Table II), indicating reduced reactivity of the macromonomer compared to the model monomer. This suggests some additional factor in copolymerization involving a macro-monomer. Repulsive interaction between different polymers[17] (polyHEMA radical and polystyrene macromonomer in this case) may possibly be such a factor.

In conclusion, copolymerization between HEMA and LMA was investigated in terms of solvent effects on the apparent monomer re-activity ratios, and discussed based on the solution properties of the monomers. Ag-gregation of hydrogen-bonding monomers in nonpolar solvents may be largely respon-sible for their increased reactivities.

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18. The peak areas (A) around $\delta 4.2$—$3.5$ come from the HEMA oxyethylene and LMA ester $\alpha$-methylene protons, while those (B) around $\delta 2.3$—$0.7$ from the other protons including the hydroxyl proton of HEMA when measured in $CDCl_3$. (In $CD_3OD$–$CDCl_3$, the HEMA hydroxyl proton merged with the peak of the solvent at $\delta 4.3$.) The mole fraction of HEMA, $x$, was obtained from the ratio $A/B$ as follows:

$A/B = [4x + 2(1-x)]/[6x + 28(1-x)]$ in $CDCl_3$,

$A/B = [4x + 2(1-x)]/[5x + 28(1-x)]$ in $CDCl_3$–$CD_3OD$.